Simulation-guided design of protocols for synthesis of soft nanoparticles via folding of single polymer chains

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Efficient folding of single polymer chains is a topic of great interest due, mainly, to the possibility of mimicking and controlling the structure and functionality of natural biomacromolecules (e.g., enzymes, drug delivery vehicles, catalysts) by means of artificial single-chain nano-objects. Unimolecular polymeric nanoparticles have already been considered in several applications as, e.g., promising elastomeric polymers, rheology agents, sensors, or smart gels. We investigate, by means of computer simulations, chemical synthesis and scattering techniques (SANS and SAXS), the formation of soft nanoparticles by irreversible intramolecular cross-linking of polymer precursors. We consider several simulation-guided design protocols, varying relevant parameters such as the number of chemical species among the linker groups (orthogonal chemistry), the linker functionality or the amphiphilicity of the precursor chains.

For synthesis in good solvent conditions, simulations reveal that the early and intermediate stages of the cross-linking process are dominated by bonding at short contour distances. The equilibrium self-avoiding character of the precursor inhibits bonding at long contour distances, which is the efficient mechanism for global compactation. Thus, irreversible cross-linking of precursors with identical molecular weight and linker fraction produces both (intrinsically polydisperse), compact and sparse objects. This is confirmed by a detailed analysis of the size and shape distribution of the fully cross-linked nanoparticles. The use of orthogonal chemistry protocols, by increasing the number of different chemical species of the linkers, lead to nanoparticles that are on average smaller and more globular than the homofunctional counterparts. We discuss the limitations of these protocols.

Cross-linking of amphiphilic precursors offers a promising alternative route for the design of globular nanoparticles. After completing synthesis in bad solvent conditions for the solvophobic part, and recovering good solvent conditions for the two species, the swollen nanoparticles result notably more compact and spherical than those obtained from purely solvophilic precursors. This protocol provides a route to design nanoparticles with specific functionalities, as e.g., nanocarriers or Janus-like catalysts.